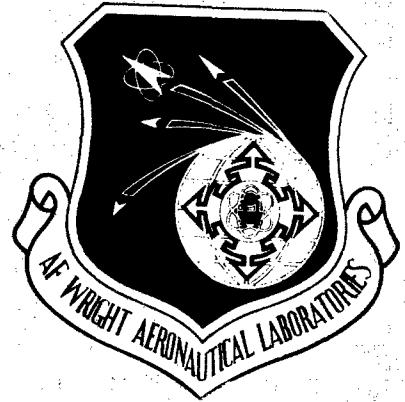


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A GENERAL PREPARATION OF TAILORED-LENGTH ACETYLENE TERMINATED
RESINS FROM LOW-COST BISPHENOLS

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This technical report has been reviewed and is approved for publication.

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for identification the major impurities present. Thermoanalytical data was obtained on the uncured and cured resins. This preparative method was also used to synthesize a monoethynyl terminated reactive diluent from 3-phenoxy-phenol.

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FOREWORD

This report was prepared by the Polymer Branch, Nonmetallic Materials Division. The work was initiated under Project No. 2419, "Nonmetallic and Composite Materials," Task No. 241904, Work Unit Directive 24190415, "Structural Resins." It was administered under the direction of the Materials Laboratory, Air Force Wright Aeronautical Laboratories, Wright-Patterson Air Force Base, Ohio, with Dr F. E. Arnold as the AFWAL/ML Work Unit Scientist. This report describes work conducted from June 1981 to December 1982.

The work described in this report was conducted by Dr F. L. Hedberg, Marilyn R. Unroe, 1st Lt Patricia M. Lindley and Marilyn E. Hunsaker. The manuscript was released by the authors in August 1983 for publication as a Technical Report.

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SECTION I

INTRODUCTION

A novel, low-cost method of preparation of acetylene terminated sulfone (ATS) resin systems was recently developed as part of an Air Force sponsored research program (References 1 and 2). The three-step method was based upon an Ullmann condensation reaction of 1,3-dibromobenzene with 4,4'-sulfonyldiphenol, followed by catalytic replacement of bromine atoms by terminal acetylene groups. The scope of this method was subsequently shown to include a number of low-cost bis-phenols (Reference 3). The various resins obtained from the method show potential as inexpensive composite matrix resins and adhesives for advanced aerospace applications where moisture insensitivity and thermooxidative stability up to 350°F are required.

The major limitation in the new preparative method occurred in the first synthetic step, where an uncontrollable mixture of different length bromine terminated oligomers was produced. Selective tailoring of the resin length was desired in order to obtain a balance between processability, toughness, and use temperature. Greater oligomeric length in acetylene terminated resins has been found to correlate with increased toughness (Reference 4). However, greater length also causes a rise in initial glass transition temperature (Tg) which hurts processability, and a fall in ultimate Tg after cure, lowering use temperature, as both Tg values converge toward the Tg of the corresponding linear polymer.

As the result of in-house research into this problem, a substantially improved modification was developed for the Ullmann condensation of 1,3-dibromobenzene and 4,4'-sulfonyldiphenol which not only afforded complete stoichiometric control of the average oligomer

length, but also afforded a significant enhancement of the yield for the reaction (Reference 5). The scope of this modification has been explored with other low-cost bis-phenols, and the results of this exploratory research are the subject of this report.

SECTION II

RESULTS AND DISCUSSION

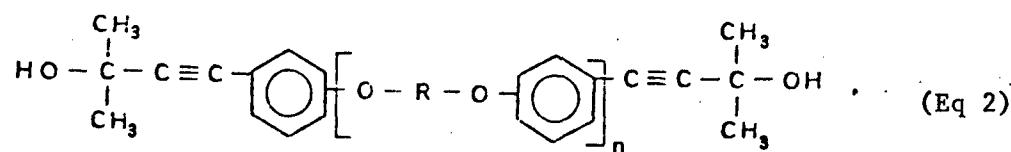
Three low-cost bis-phenols, resorcinol, bis-phenol A, and 4,4'-thiodiphenol, were reacted in varying stoichiometric ratios with either 1,3-dibromobenzene or 1,4-dibromobenzene, and cuprous oxide in 2,4,6-collidine, under conditions similar to those previously reported for the preparation of the ATS resin systems (Reference 5), to form bromine terminated oligomers as shown in eq. 1. The conditions used for these Ullmann type reactions, and the results therefrom, are compiled in Table 1. Conversion of some of the bromine terminated oligomer mixtures to the corresponding acetylene terminated mixtures was carried out as shown in eq. 2 and 3, utilizing conditions similar to those previously described for the ATS systems (References 1 and 2). The overall yields for the bromine to acetylene conversion together with thermomechanical characterization data are shown in Table 2. Generic acronyms applied to these resin systems are ATP: resorcinol-based; ATB: bis-phenol A-based; and ATT: 4,4'-thiodiphenol-based.



Cu_2O \downarrow 2, 4, 6 - Collidine



Et_3N \downarrow $\text{HC}\equiv\text{CC}(\text{CH}_3)_2\text{OH}$
 $\quad\quad\quad$ $\downarrow (\text{P}_3\text{P})_2\text{PdCl}_2 \quad \text{CuI}$



NaOH \downarrow toluene

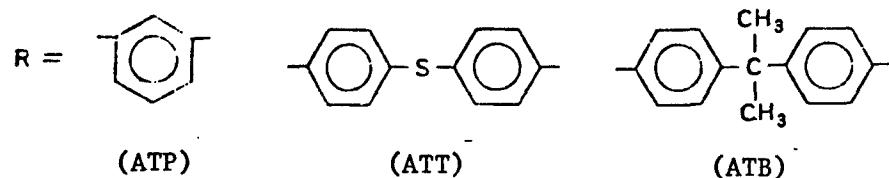
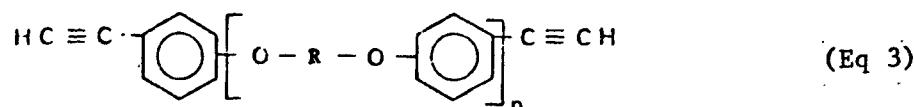


TABLE 1

ULLMANN REACTION CONDITIONS AND RESULTS

Type of Bis-Phenol	Dibromobenzene: Bis-Phenol Mole Ratio	Reaction Time/hrs	% Yield ^c	$\frac{n=1}{n>1}$
BPA	20:1 ^a	19.5	93	94/6
BPA	10:1 ^a	20.5	89	89/11
BPA	10:1 ^b	17	64	89/11
BPA	4:1 ^a	67	81	60/40
BPA	2:1 ^a	72	64	23/77
BPA	2:1 ^b	49	76	40/60
TDP	10:1 ^a	8	83	77/23
TDP	10:1 ^b	20	70	87/13
TDP	4:1 ^a	10	77	60/40
TDP	2:1 ^a	93	65	22/78
RES	10:1 ^a	18	80	85/15
RES	2:1 ^a	21	49	45/55

Key: BPA: Bis-phenol A

TDP: 4,4'-thiodiphenol

RES: Resorcinol

a: 1,3-dibromobenzene used

b: 1,4-dibromobenzene used

c: Yields were determined by column chromatographic isolation and gravimetric analysis of n=1, n=2, and n>2 components, with the molecular weight of the n>2 component approximated as the n=3 component.

TABLE 2

YIELDS AND Tg VALUES FOR CONVERSION OF BROMINE TERMINATED OLIGOMERS
TO ACETYLENE TERMINATED OLIGOMERS

	<u>n=1/n>1</u>	<u>% yield</u>	<u>Tg init^c</u>	<u>Tg cured</u>
ATB ^a	89/11	79	-5	265 ^{d, g}
	52/48	66	-11	202 ^{e, h}
	23/77	44	1	160 ^{d, h}
ATB ^b	89/11	64	1	
	40/60	57	2	
ATP ^a	100/0	76		
ATT ^a	100/0 ^k	--	-25	347 ^{e, i}
	75/25	76	-26	168 ^{f, j}
	60/40	75	-14	144 ^{f, j}
	22/78	57	5	112 ^{f, j}
ATT ^b	100/0 ^k	--	156 (T _g)	none ^{f, i}
	97/3	52	138 (T _m)	

- a. from 95% 1,3-dibromobenzene/5% 1,4-dibromobenzene
- b. from 1,4-dibromobenzene
- c. samples contain some residual solvent
- d. by TICA
- e. by TMA
- f. by DSC
- g. cured 4 hrs @ 250°C in N₂
- h. cured 16 hrs @ 218°C in N₂
- i. cured 8 hrs @ 287°C under vacuum
- j. heated in DSC to 450°C and recycled
- k. obtained by column chromatography from oligomer mixture

A preparation of ATP and ATT resins has been previously reported (Reference 3). The new method of synthesis, however, affords both substantially improved yields and control of oligomer length which was not obtained in the earlier work. The ATB resins have not been previously reported.

Yields at high dibromobenzene/bis-phenol ratios were very good for all three resin systems as had been found with bromine terminated ATS. Reaction times were faster than with ATS, however, indicating that the three bis-phenols used were more reactive than 4,4'-sulfonyldiphenol under the Ullmann reaction conditions employed. Further evidence of this enhanced reactivity can be seen in the yields obtained at 2:1 stoichiometry which were at least twice as great as obtained for ATS. This result permitted a variation in the ratio of $n=1/n>1$ components in the product, as determined by chromatographic analysis, from 9:1 to 1:4. The $n=1/n>1$ ratio was chosen as an easily obtained measure of oligomer length from column chromatographic analysis.

One problem which occurred at the lower $n=1/n>1$ ratios was the formation of small amounts of product with a single bromine atom. This product was not discernible by TLC analysis until after reaction with 2-methyl-3-butyn-2-ol (eq.2) with which it forms a series of oligomeric mono-adducts, easily separable by chromatography from the bis-adducts. Leaving the mono-adducts in the mixture at this point will result in an inseparable mixture of mono-ethynyl terminated oligomers in the final resin after cleavage of acetone (eq.3), but retention would be preferable economically. The presence of 5-10% of the mono-acetylene terminated component (1-[3-ethynylphenoxy]-3-phenoxybenzene) in acetylene terminated quinoxaline (ATQ) resins has been found to be beneficial for processing properties without hurting mechanical properties (Reference 6 and 7).

Whether or not this is true for the ATP, ATB and ATT resins will have to be determined. The increased amounts of mono-adduct formed at the lower $n=1/n>1$ ratios may be due to slower formation of the $n>1$ components permitting reductive debromination as a side reaction to become more competitive. TLC analysis of progress of the Ullmann ether reaction indicated the initial formation of the $n=1$ component to be significantly more rapid than subsequent formation of the $n>1$ components. This effect can be attributed both to the lower amount of dibromobenzene present at later stages of the reaction and possibly to lower solubility of the larger copper complex intermediates required for formation of the $n>1$ components.

For composite applications requiring a maximum use temperature of 177°C, a minimum Tg after cure of 220°C was desired. Additionally, an initial Tg below ambient temperature was desired for melt processability and for a substantial window between the initial Tg and the onset of cure.

Initial Tg values should increase within an AT resin family with increasing molecular size. By contrast, Tg after cure values should decrease with increasing molecular size because of lesser crosslink density. Thus, as the $n=1/n>1$ ratio decreases, the Tg before cure and the Tg after cure should converge toward the Tg of the corresponding high molecular weight polymer. To some extent this trend can be seen in Table 2. Accurate initial Tg values were difficult to obtain because of problems with solvent removal from some of the samples, while after cure Tg values were obtained by differing curing cycles and measurement techniques.

The high Tg after cure values required for 177°C applications were obtained in the ATB systems only at high $n=1/n>1$ ratios for the

1,3-dibromobenzene based systems. By contrast, satisfactory high after cure Tg values were obtained over a wide range of $n=1/n>1$ ratios for all the 1,4-dibromobenzene based systems. The increase in rigidity obtained by changing the ends of the molecule from a meta to a para orientation would be expected to provide a corresponding increase in Tg after cure. What is surprising is the large degree of enhancement of after cure Tg obtained for the lower $n=1/n>1$ ratios where the enhancement in rigidity pertains only to a relatively small percent of the molecule.

In the ATT systems, very low after cure Tg values were obtained for the 1,3-dibromobenzene based materials except for the composition with no $n>1$ components present. Comparison of the range of these values with the range for the corresponding 1,3-dibromobenzene based ATB compositions indicates a substantially greater flexibility for the thioldiphenylene linkage versus the isopropylidenediphenylene linkage.

The only ATT system prepared from 1,4-dibromobenzene contained none of the $n>1$ components and showed no indication of a Tg after cure. A major drawback to this material, however, was the presence of a crystalline melting point at 156°C which could cause severe processing problems.

Two different methods for potentially increasing toughness in a thermoset resin are to increase the average oligomer length, thus increasing the distance between crosslinks, or to increase the flexibility of the backbone structure. The drawbacks to the former method are the corresponding increase in initial Tg and decrease in cured Tg with increasing length as discussed previously. The drawback to the latter method is the corresponding decrease in cured Tg with increasing flexibility. Comparative mechanical properties evaluation of some of the resins shown in Table 2 should provide

some insight into the correlation between crosslink density and backbone flexibility, and toughness. Some preliminary results of this evaluation have been reported (References 8 and 9).

Isothermal ageing in air at 260°C was carried out on a 1,3-dibromobenzene base, ($n=1/n>1$) = 85/15 sample of ATB which had been cured for 16 hours at 218°C under nitrogen. After 78 hours, only a 2% weight loss was noted. The temperature was raised to 316°C, causing a marked increase in rate of weight loss, with 19% additional weight loss over a 13 hour period.

A 1,4-dibromobenzene based ($n=1/n>1$) = 100/0 sample of ATT which had been cured for 8 hours at 287°C under vacuum was isothermally aged in air at 316°C. Ninety-four hours were required to attain 19% weight loss, and 42% weight loss was observed after 200 hours.

The difference between the ATB and ATT samples can be attributed either to greater stability of the thioether linkage versus the isopropylidene linkage or to greater stability of the crosslinking site derived from a para ethynyl group versus a meta ethynyl group. While the former explanation is the more likely, further isothermal ageing comparisons will be necessary to draw a more definite conclusion.

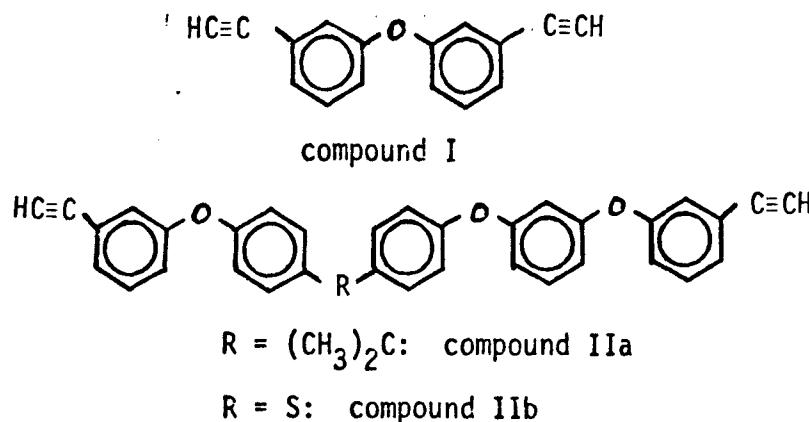
Interest in the ATP resins has centered on their use as reactive plasticizers for ATQ resins analogous to the previously described utilization of 1-(3-ethynylphenoxy)-3-phenoxybenzene (References 6, 7, and 10). For this purpose, it was most desirable to maximize the amount of $n=1$ product which was purified by distillation at the bromine terminated stage before conversion to ATP. As shown in Table 1, an 80% yield of purified 1,3-bis(bromophenoxy)benzene was obtained from the Ullmann reaction. The amount of $n>1$ oligomers obtained in this case was approximated from the

weight of the residue in the still after distillation. It was also found that a 76% yield of bromine terminated ATP was obtained when the Ullmann reaction was carried out in collidine with CuO instead of Cu₂O.

The new synthetic method was also applied to the synthesis of 1-(3-ethynylphenoxy)-3-phenoxybenzene using 3-phenoxyphenol, 1,3-dibromobenzene, and Cu₂O in 2,4,6-collidine. An 87% yield of 1-(3-bromophenoxy)-3-phenoxybenzene was obtained after distillation, and this was converted to the acetylene terminated product in 72% overall yield.

As noted previously, the formation of the bromine terminated oligomers was accompanied by the formation of small amounts of mono-bromo derivatives which were distinguishable only after reaction with 2-methyl-3-butyn-2-ol. The mono-adduct formed in this reaction was separable by thin layer or column chromatography due to the distinct polarity of the tertiary alcohol. Small amounts of other impurities with R_f values immediately higher than the monomer and with R_f values between monomer and dimer were distinguished during TLC analysis of the bromine terminated oligomers. When isolation of these components by column chromatography was performed it was found that additional components were obtained with R_f values so near the monomer as to be indistinguishable upon elution on a TLC strip (1:1 hexane:chloroform). The depth of the trials was limited due to the paucity of crude material available with which to work and the limitations of the Finnegan 4021 GC/MS/DS mass spectrometer used to characterize compounds of molecular weight greater than 600 g/mol. However, the compounds were identified as components in both the bromine terminated (Table 5) and acetylene terminated oligomers (Tables 3 and 4), and the use of 1,3-dibromobenzene versus 1,4-dibromobenzene did not influence the

magnitude of the presence of these compounds. Some of the compounds present in the largest quantities in ATB mixtures derived from 1,3-dibromobenzene include 3,3'-diethynylidiphenylether (compound I) and 2,2'-[4-(3-ethynylphenoxy)phenyl-4'-(3-[3-ethynylphenoxy]-phenoxy)phenyl]-propane (compound IIa). The sulfide analog (compound IIb) of compound IIa was identified as well as the para substituted analogs of compounds I, IIa and IIb in ATB and ATT mixtures derived from 1,4-dibromobenzene.



In the ATB systems the amount of compound I ranged from 1% to 3% by weight while the amount of compound IIa was found as low as 1% to as high as 10% of the total sample weight. The amount of these compounds can be reduced by azeotroping some of the collidine and water initially generated although complete removal of these compounds was not possible regardless of the amount of azeotroping done. The representative column chromatographs of an ATB resin, ATT resin and the bromine terminated precursor to an ATT resin (Tables 3, 4 and 5) summarize the isolation of some of these compounds and their characterization by mass spectrometry.

TABLE 3

SUMMARY OF A REPRESENTATIVE COLUMN CHROMATOGRAPH OF ATB/OATB
 FROM 95/5 1,3-DIBROMOBENZENE/1,4-DIBROMOBENZENE WITH $[n=1/n>1] = 27/73$

Fraction No.	Eluant	Dry Wt. (g)	Mass Spectrum <u>M+1(M/Z)</u>	Compound
1	cyclohexane	0.01	219	Ib
2	cyclohexane	0.01	-	-
3	"	0.01	311	ATP
4	"	negl.	311	ATP
5-8	4:1 cyclohexane:CCl ₄	0.10	429	ATB
9	2:1 cyclohexane:CCl ₄	0.03	-	-
10	CCl ₄	0.11	511	IIa
11	"	0.06	-	-
12	"	0.06	-	-
13	"	0.02	-	-
14	CHCl ₃	0.05	-	-
15	THF	0.01	-	-

TABLE 4

SUMMARY OF A REPRESENTATIVE COLUMN CHROMATOGRAPH
 OF para-ATT/OATT (FROM 1,4-DIBROMOBENZENE WITH $[n=1/n>1] = 97/3$)

Fraction No.	Eluant	Dry Wt. (g)	Mass Spectrum <u>M⁺</u>	Compound
1-2	1:1 cyclohexane:CCl ₄	0.58	218,	I (para)
3-7	"	3.99	418	ATT
8-13	"	0.96	510	IIb (para)
14-15	CCl ₄	0.43	418, 510	ATT, IIb (para)
16	"	0.11	418, 510	" , "
17	CHCl ₃	0.12	-	-
18	THF	0.17	-	-

TABLE 5

SUMMARY OF REPRESENTATIVE COLUMN CHROMATOGRAPH OF BATT/OBATT
 A BROMINE TERMINATED ATT PRECURSOR
 (FROM 95/5 1,3-DIBROMOBENZENE/1,4-DIBROMOBENZENE WITH $[n=1/n>1] = 75/25$)

Fraction No.	Eluant	Dry Wt. (g)	M+1	Mass Spectrum (CIMS, Methane) Compound
1	cyclohexane	0.03	329	I (Br terminated)
2-4	"	0.24	529	ATT (Br terminated)
5-6	"	0.01	621	IIb (Br terminated)
7-10	2:1 CCl_4 :cyclohexane	0.06	621	IIb (Br terminated)
11	CCl_4	0.04	-	-
12	"	0.04	-	-
13	"	0.01	-	-
14	"	0.01	-	-
15	CHCl_3	0.02	-	-

SECTION III

CONCLUSIONS

The new method for synthesis of acetylene terminated oligomers described herein appears to be quite general for various bis-phenols or mono-phenols. Further modifications of the method should enhance its potential for economical manufacture. Suggested modifications include the following:

1. Use in the Ullmann ether step of a catalytic amount of cuprous oxide together with a stoichiometric amount of sodium oxide or sodium carbonate would afford soluble sodium bromide instead of insoluble copper bromide and facilitate both the reaction work-up and waste products disposal.
2. Use of a polymer suspended tetrakis triphenyl phosphine palladium catalyst for the second step of the reaction would permit reuse of the catalyst as well as eliminate the need for a catalyst removal operation or a triphenylphosphine removal operation in the work-up.
3. If a polymer suspended palladium catalyst is not successful, the necessary palladium removal step could be facilitated by using an ion-exchange type column containing complexing agents such as ethylenediamine or 2,2'-bipyridine attached to a polymer.
4. An ion-exchange column containing a quaternizing agent such as methyl iodide could be used for removal of triphenylphosphine. A successful quaternization based removal of triphenylphosphine from ATB has been reported from a recent contractual effort (Reference 11).
5. Replacement of carbon tetrachloride as a work-up solvent in the Ullmann ether reaction would be necessary for safety reasons.

Toluene-cyclohexane mixtures may be found with similar solvating ability. An alternative approach which could be used for resins consisting solely of the $n=1$ component would be vacuum distillation of the bromine terminated $n=1$ component.

The new method of synthesis was most successful from a standpoint of both yield and purity with resins containing a high ratio of $n=1/n>1$ components. The most promising materials with respect to processability and use temperature were, in fact, the 1,3-dibromobenzene based ATB and ATT resins with the highest ratios of $n=1/n>1$ components. High $n=1/n>1$ ratio ATB resins have been determined to be easily processable and to be tougher than the corresponding ATS resins (References 8 and 9): The very high $n=1/n>1$ ratio ATT resins displayed the greatest range of T_g values ($-25^\circ\text{C} - 347^\circ\text{C}$ for $n=1/n>1 = 100/0$) and, as discussed earlier, appear to be more flexible (and thus possibly tougher) than the ATB resins, therefore warranting further evaluation. The third promising material obtained this study was the low $n=1/n>1$ ratio ATB system based upon 1,4-dibromobenzene. The major advantage of this system, currently under evaluation, is the inherent toughness expected from the greater average oligomer length. A second advantage, the significantly lower cost of 1,4-dibromobenzene versus 1,3-dibromobenzene, is expected to be only temporary since a planned large scale manufacture of 1,3-dibromobenzene should make the prices more comparable (References 12). The major synthetic difficulty with the 1,4-dibromobenzene based systems seems to be a significant slowing of the reaction beyond the $n=1$ stage versus the 1,3-dibromobenzene based systems. Formation of $n=1$ components was roughly comparable in rate for both 1,3- and 1,4-dibromobenzene. This difficulty could be due to lower solubility of the 1,4- substituted copper complex intermediates. If this is the case, a mixed solvent system such as N,N-dimethylacetamide-2,4,6-collidine may be useable.

SECTION IV

EXPERIMENTAL

1. Instrumentation

Proton nuclear magnetic resonance (^1H NMR) spectra were recorded on a Varian EM-360A spectrometer using 10% weight/volume solutions in deuteriochloroform (Aldrich 99.6% gold label) with tetramethylsilane as an internal standard. Melting points were obtained using a Mel-Temp capillary melting point apparatus. Elemental analyses and mass spectra (EIMS and CIMS) were performed by the Analytical Branch of the Air Force Wright Aeronautical Laboratories, WPAFB, OH. The mass spectra were performed on a Finnegan 4021 GC/MS/DS using a methane purge for CIMS and trailer gases from the gas chromatograph for EIMS. Glass transition temperatures (T_g 's) were determined by differential scanning calorimetry (DSC) on a Dupont 990 using a nitrogen purge.

2. General Preparation of Bromine Terminated Oligomers from 4,4'-thiodiphenol or bis-phenol A

The appropriate molar amounts (see Table 1) of either 4,4'-thiodiphenol or bis-phenol A and either 1,3-dibromobenzene or 1,4-dibromobenzene were combined with cuprous oxide (2 x the molar quantity of bis-phenol) and 2,4,6-collidine (6 x the molar quantity of bis-phenol). The mixture was stirred vigorously and heated at 170° until TLC analysis indicated the absence of both starting bis-phenol and monosubstituted phenol. Work-up and $n=1/n>1$ ratio determinations were carried out as previously described for ATS (Reference 5). Satisfactory analyses were obtained for the $n=1$ derivatives from both bis-phenols.

3. Preparation of 1,3-bis(3-bromophenoxy)benzene and 1-(3-bromophenoxy)-3-phenoxybenzene was carried out using a 10:1 molar ratio of 1,3-dibromobenzene to either resorcinol or 3-phenoxyphenol. The procedure was the same as described above except that hexane was used in place of carbon tetrachloride during the work-up, and the products were distilled. 1,3-bis(3-bromophenoxy)benzene boiled at 225°C at 0.65mm. 1-(3-bromophenoxy)-3-phenoxybenzene boiled at 215°C at 2.5mm. Satisfactory analyses were obtained on both compounds. For one preparation of 1,3-bis(3-bromophenoxy)benzene, cuprous oxide was replaced by an equivalent amount of cupric oxide.

4. Conversion of Bromine Terminated Oligomers to Acetylene Terminated Oligomers was carried out as described for ATS (References 1 and 2). With the 2:1 dibromobenzene:bis-phenol products, it was found more convenient for transfer to dissolve the bromine terminated oligomers in 1 part of pyridine and dilute with 2 parts of triethylamine. The presence of pyridine did not appear to influence the yield when compared with using triethylamine alone.

Tg values for the acetylene terminated resins (Table 2) were determined by TMA analysis under nitrogen at 10°C per minute. Samples of acetylene terminated resins were cured as described in the footnotes to Table 2.

5. Chromatograph of ATB based on 95/5 1,3-dibromobenzene/1,4-dibromobenzene

A sample of ATB was prepared according to the previously mentioned experimental procedures and a portion (0.47g) was chromatographed on a silica gel column (Woelm DCC, 45.6g, 2cm dia x 28cm L) using the eluant scheme listed in Table 3. Mass balance was achieved

after evaporation and drying of the fractions in a 50°C oven under reduced pressure of 2 h. The $n=1/n>1$ (wt. ratio) was determined to be 27/73.

Analysis of compound I: mass spectrum (CIMS) (relative intensity):
M/Z 247 (16, M+29), 219 (100, M+1), 130 (15).

Analysis of ATP: mass spectrum (CIMS), M/Z (relative intensity) 339 (17, M+29), 311 (100, M+1), 283 (10, M-27).

Analysis of ATB (n=1): oil; Anal. Calc'd for $C_{31}H_{24}O_2$: C, 86.88; H, 5.66. Found: C, 86.67, 86.41; H, 5.77, 5.75; mass spectrum (CIMS), M/Z (relative intensity) 457 (13, M+29), 429 (83, M+1), 235 (100, M- $\text{H}_2\text{O}\text{C}\equiv\text{CH}$).

Analysis of compound IIa: mass spectrum (CIMS), M/Z (relative intensity) 549 (1, M+29), 521 (14, M+1), 327 (4, M- $\text{H}_2\text{O}\text{C}\equiv\text{CH}$), 235 (100, M- $\text{H}_2\text{O}\text{C}\equiv\text{CH}$).

Analysis of ATB (n=2): oil; Anal. Calc'd for $C_{52}H_{42}O_4$: C, 85.48; H, 5.75. Found: C, 84.26, 84.70, 85.21; H, 5.66, 5.76, 5.79.

Analysis of ATB (n=3): oil; Anal. Calc'd for $C_{73}H_{60}O_6$: C, 84.88; H, 5.81. Found: C, 82.97, 82.02; H, 5.98, 5.76.

6. Chromatograph of ATT based on 1,4-dibromobenzene

The crude ATT (7.04g) which was prepared according to previously noted experimental procedures was suspended in 1:1 cyclohexane:CCl₄ with some heating and chromatographed on a silica gel column (Woelm DCC, 273g, 5cm dia x 30cm L) using the eluant scheme listed in Table 4. Like fractions were combined, evaporated to dryness, and dried in a 70°C oven under reduced pressure for 4 h. Mass balance was not achieved; however, the dry weights after chromatography accounted for 90% of the crude material. The $n=1/n>1$ (wt. ratio) was determined to be 97/3.

Analysis of compound I (para): mass spectrum (EIMS), M/Z (relative intensity) 218 (100, M⁺), 189 (45, M-CHO), 163 (5-M-C₂H₂), 118 (10, p-HOOC \equiv CH), 101 (23, $\text{C}\equiv\text{C}^+$).

Analysis of ATT (para, n=1): mp 150-152°C; ^1H NMR 6.8-7.5 (dd, aromatic, 16H), 3.1 (s, methine, 2H); mass spectrum (EIMS), M/Z (relative intensity) 418 (100, M^+), 301 (23, $\text{M}-\text{p}-\text{OOC}\equiv\text{CH}$), 285 (18.5, $\text{M}-\text{S}-\text{OC}\equiv\text{CH}$), 209 (49.5, M^{++}), 184 (57.5, $\text{C}_6\text{H}_4-\text{S}-\text{C}_6\text{H}_4$), 171 (35, 184-CH), 101 (65, $\text{C}_6\text{H}_4\text{C}\equiv\text{CH}^+$), 75 (44, C_6H_3^+); Anal. Calc'd for $\text{C}_{28}\text{H}_{18}\text{O}_2\text{S}$: C, 80.46; H, 4.31; S, 7.66. Found: C, 77.91, 78.54, 79.00; H, 4.26, 4.26, 4.34; S, 7.40, 7.58.

Analysis of compound IIb (para): mass spectrum (EIMS), M/Z (relative intensity) 510 (100, M^+).

7. Chromatograph of ATT (Bromine Terminated) Based on 95/5

1,3-dibromobenzene/1,4-dibromobenzene

A crude ATT (bromine terminated) mixture was prepared according to the general preparation of bromine terminated oligomers by using a 95/5 isomeric mixture of meta/para-dibromobenzene and 4,4'-thiodiphenol. A sample (0.50g) of the mixture was chromatographed on a silica gel column (Woelm DCC, 40.71g, 2cm dia x 25 cm L) using the eluant scheme listed in Table 5. Mass balance was not achieved, but 92% recovery of the products was realized. Similar fractions were combined and dried in a 40°C oven for 4 h under reduced pressure and 60°C for 2 h under reduced pressure. The n=1/n>1 (wt. ratio) was determined to be 75/25.

Analysis of compound I (Br terminated): mass spectrum (CIMS), M/Z (relative intensity) 359 (16, $\text{M}+29$, $^{81}\text{Br}^{81}\text{Br}$), 357 (18.5, $\text{M}+29$, $^{81}\text{Br}^{79}\text{Br}$), 355 (2, $\text{M}+29$, $^{79}\text{Br}^{79}\text{Br}$), 331 (38, $\text{M}+1$, $^{81}\text{Br}^{81}\text{Br}$), 329 (78, $\text{M}+1$, $^{81}\text{Br}^{79}\text{Br}$), 327 (41, $\text{M}+1$, $^{79}\text{Br}^{79}\text{Br}$), 251 (50, $\text{M}-\text{Br}+2\text{H}$, ^{81}Br), 249 (50, $\text{M}-\text{Br}+2\text{H}$, ^{79}Br).

Analysis of ATT (Br terminated, n=1): crystallized from CH_2Cl_2 /hexane, colorless needles, mp 62-63°C; ^1H NMR 6.9-7.5 (m, aromatic, 16H); mass spectrum (EIMS), M/Z (relative intensity) 530 (92, M^+ , $^{81}\text{Br}^{81}\text{Br}$), 528 (100, M^+ , $^{81}\text{Br}^{79}\text{Br}$), 526 (27, M^+ , $^{79}\text{Br}^{79}\text{Br}$), 357 (12, $\text{M-Br}\emptyset\text{O}^+$, ^{81}Br), 355 (11, $\text{M-Br}\emptyset\text{O}^+$, ^{79}Br), 341 (6, $\text{M-S-Br}\emptyset^+$, ^{81}Br), 339 (6, $\text{M-S-Br}\emptyset^+$, ^{79}Br), 184 (47, $\text{C}_6\text{H}_4\text{S}^+\text{C}_6\text{H}_4$), 171 (50, 184-CH), 157 (26, $\text{C}_6\text{H}_4\text{Br}$, ^{81}Br), 155 (26, $\text{C}_6\text{H}_4\text{Br}^+$, ^{79}Br), 139 (36, 171-S); Anal. Calc'd for $\text{C}_{24}\text{H}_{16}\text{O}_2\text{SBr}_2$: C, 54.55; H, 3.03; S, 6.07; Br, 30.30. Found: C, 54.71, 54.50; H, 3.14, 3.13; S, 6.07, 6.08; Br, 29.56, 30.15, 29.20, 29.20.

Analysis of compound IIb (Br terminated): mass spectrum (CIMS), M/Z (relative intensity) 651 (9, $\text{M}+29$, $^{81}\text{Br}^{81}\text{Br}$), 649 (14, $\text{M}+29$, $^{81}\text{Br}^{79}\text{Br}$), 647 (7, $\text{M}+29$, $^{79}\text{Br}^{79}\text{Br}$), 623 (47, $\text{M}+1$, $^{81}\text{Br}^{81}\text{Br}$), 622 (31, M^+ , $^{81}\text{Br}^{81}\text{Br}$), 621 (68, $\text{M}+1$, $^{81}\text{Br}^{81}\text{Br}$), 620 (35, M^+ , $^{81}\text{Br}^{79}\text{Br}$), 619 (38, $\text{M}+1$, $^{79}\text{Br}^{79}\text{Br}$), 618 (38, M^+ , $^{79}\text{Br}^{79}\text{Br}$), 541 (30, M-Br , ^{81}Br), 539 (12, M-Br , ^{79}Br), 461 (24, 539-Br+H), 373 (94, $\text{M-}\emptyset\text{O}\emptyset\text{Br}$, ^{81}Br), 371 (100, $\text{M-}\emptyset\text{O}\emptyset\text{Br}$, ^{79}Br), 293 (19, 371-Br+H), 281 (54, $\text{M-}\emptyset\text{O}\emptyset\text{O}\emptyset\text{Br}$, ^{81}Br), 279 (54, $\text{M-}\emptyset\text{O}\emptyset\text{O}\emptyset\text{Br}$, ^{79}Br), 83 (75, HBr+H , ^{81}Br), 81 (80, HBr+H , ^{79}Br).

Analysis of ATT (Br terminated, n=2): colorless oil; Anal. Calc'd for $\text{C}_{42}\text{H}_{28}\text{O}_2\text{S}_2\text{Br}_2$: C, 61.46; H, 3.41; S, 7.80; Br, 19.51. Found: C, 61.19, 61.36; H, 3.55, 3.54; S, 7.32, 7.06, 7.60; Br, 18.88, 18.93.

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